

A Study on the Formation of Complex Compounds
between Bivalent and Univalent Salts. V

**Systems: $\text{Hg}(\text{CN})_2\text{-MX-H}_2\text{O}$
($\text{X} = \text{Cl, Br or CNS}$ and $\text{M} = \text{NH}_4$ or Li)**

By A. K. AGRAWAL and R. C. MEHROTRA

Abstract

A preparative study of the systems: $\text{Hg}(\text{CN})_2\text{-MX-H}_2\text{O}$ (where $\text{X} = \text{Cl, Br or CNS}$ and $\text{M} = \text{NH}_4$ or Li) has been carried out and complexes of the type $\text{MHg}(\text{CN})_2\text{X}$ (or $\text{MHg}(\text{CN})_2\text{X} \cdot x\text{H}_2\text{O}$) have been isolated. Further, it has been concluded that the chloride complexes are the least stable.

The mercury halide complexes of the type $(\text{HgX}_3)^-$ and $(\text{HgX}_4)^{--}$ are well known since long but the mixed halide-pseudohalide complexes of mercury although studied earlier¹⁻⁴), have received considerable attention only for the last few years⁵⁻⁶). The authors⁷⁻⁹) have recently carried out a preparative study of the systems: $\text{HgX}_2\text{-MCN-H}_2\text{O}$ and $\text{Hg}(\text{CN})_2\text{-MX-H}_2\text{O}$ (where $\text{X} = \text{Cl, Br or CNS}$ and $\text{M} = \text{K or Na}$) and have isolated three different types of complexes MHgX_2CN , $\text{MHg}(\text{CN})_2\text{X}$ and $\text{M}_2\text{Hg}(\text{CN})_4$ from the potassium systems whereas from the sodium systems the only complex which could be isolated corresponded to the formula $\text{MHg}(\text{CN})_2\text{X}$. In this investigation, the above study has been extended to the systems: $\text{Hg}(\text{CN})_2\text{-MX-H}_2\text{O}$ (where $\text{M} = \text{NH}_4$ or Li) and complexes of the type $\text{MHg}(\text{CN})_2\text{X}$ (or $\text{MHg}(\text{CN})_2\text{X} \cdot x\text{H}_2\text{O}$) have been isolated. The order of stability already pointed out in Part III⁸) of the series has also been confirmed.

¹) R. VARET, Ann. Chim. Phys., (7) 8, 278 (1896).

²) E. RUFF and S. GOY, Arch. Pharm., 247, 100 (1909).

³) F. BOURION and E. ROUYER, Ann. Chim., 10, 263 (1928).

⁴) G. DENIGES, Compt. rend., 213, 604 (1941); Chem. Zentr., 1, 2244 (1942).

⁵) R. C. AGGARWAL and R. C. MEHROTRA, Z. anorg. allg. Chem., 297, 65 (1958).

⁶) R. A. PENNEMAN and L. H. JONES, J. Inorg. Nuclear Chem., 20, 19 (1961).

⁷) A. K. AGRAWAL and R. C. MEHROTRA, Z. anorg. allg. Chem., 312, 230 (1961).

⁸) A. K. AGRAWAL and R. C. MEHROTRA, Z. anorg. allg. Chem., in press.

⁹) A. K. AGRAWAL and R. C. MEHROTRA, Z. anorg. allg. Chem., in press.

Experimental

Materials. B. D. H. and E. MERCK chemicals (Laboratory Reagent) were used for the preparative work.

Analytical Methods. MERCURY was estimated as sulfide. HALIDE was estimated by holding cyanide in solution with formaldehyde and precipitating with silver nitrate. THIOCYANATE was oxidised to sulfate with bromine water and estimated as barium sulfate. CYANIDE was estimated by conversion to bromine cyanide with bromine water, removing excess bromine with phenol, adding potassium iodide which liberated an equivalent amount of iodine which was titrated against thiosulfate using starch as indicator. In case of thio-cyanate compounds, this method gave the total cyanide and thiocyanate from which the amount of cyanide was calculated with the help of thiocyanate determined separately.

Preparative Experiments and Results

Products obtained from reaction mixtures having different molecular ratio of the reactants, namely $\text{Hg}(\text{CN})_2$ and MX in concentrated aqueous solutions have been analysed. In all cases, the compounds crystallised out in the form of white needles soluble in water and corresponded to the general formula $\text{MHg}(\text{CN})_2\text{X}$ (or $\text{MHg}(\text{CN})_2\text{X} \cdot x\text{H}_2\text{O}$). The lithium compounds are remarkably hygroscopic and could be crystallised out with great difficulty. Further, the anhydrous compound was obtained only when the drying was done at a temperature of 110°C , otherwise a hydrated product was obtained. In the table below are summarised the analyses of various products obtained from different molar ratio of the reactants.

Molar ratio of the reaction mixture	Analysis of the product			Yield
	Hg	CN	X	
1. $\text{Hg}(\text{CN})_2 \cdot \text{NH}_4\text{Cl}$	66.3	16.2	10.4	35.0%
2. $\text{Hg}(\text{CN})_2 \cdot 2 \text{NH}_4\text{Cl}$	65.1	16.0	11.2	35.0%
3. $\text{Hg}(\text{CN})_2 \cdot 4 \text{NH}_4\text{Cl}$	65.9	16.0	11.1	7.0%
$\text{NH}_4\text{Hg}(\text{CN})_2\text{Cl}$ requires:	65.5	17.0	11.6	
4. $\text{Hg}(\text{CN})_2 \cdot \text{NH}_4\text{Br}$	58.3	14.4	23.1	33.0%
5. $\text{Hg}(\text{CN})_2 \cdot 2 \text{NH}_4\text{Br}$	57.5	14.3	23.2	55.0%
6. $\text{Hg}(\text{CN})_2 \cdot 4 \text{NH}_4\text{Br}$	57.8	14.3	23.5	45.0%
$\text{NH}_4\text{Hg}(\text{CN})_2\text{Br}$ requires:	57.1	14.8	22.8	
7. $\text{Hg}(\text{CN})_2 \cdot \text{NH}_4\text{CNS}$	60.9	14.8	18.8	72.0
8. $\text{Hg}(\text{CN})_2 \cdot 2 \text{NH}_4\text{CNS}$	61.7	14.7	18.4	90.0%
9. $\text{Hg}(\text{CN})_2 \cdot 4 \text{NH}_4\text{CNS}$	60.7	14.7	18.3	87.0%
$\text{NH}_4\text{Hg}(\text{CN})_2\text{CNS}$ requires:	60.9	15.8	17.7	
10. $\text{Hg}(\text{CN})_2 \cdot \text{LiCl}$	78.6	18.7	nil	
Calc. for $\text{Hg}(\text{CN})_2$:	79.3	20.7		
11. $\text{Hg}(\text{CN})_2 \cdot 2 \text{LiCl}$	68.7	15.8	11.3	27.0%
12. $\text{Hg}(\text{CN})_2 \cdot 4 \text{LiCl}$	68.9	15.7	10.9	22.0%
$\text{LiHg}(\text{CN})_2\text{Cl}$ requires:	67.9	17.6	12.0	
13. $\text{Hg}(\text{CN})_2 \cdot \text{LiBr}$	50.3	13.0	19.2	10.0%
14. $\text{Hg}(\text{CN})_2 \cdot 2 \text{LiBr}$	49.1	12.9	19.8	45.0%
15. $\text{Hg}(\text{CN})_2 \cdot 4 \text{LiBr}$	57.8	15.0	22.7	30.0%
$\text{LiHg}(\text{CN})_2\text{Br} \cdot 3 \text{H}_2\text{O}$ requires:	50.9	13.2	20.3	and
$\text{LiHg}(\text{CN})_2\text{Br}$ requires:	59.0	15.3	23.6	

Dehydration of $\text{LiHg}(\text{CN})_2\text{Br} \cdot 3 \text{H}_2\text{O}$

The compound was heated to constant weight at 110°C and analysed when it was found to lose water.

Found: Hg 58.1, CN 15.0, Br 23.2%
LiHg(CN)₂Br requires: 59.0, 15.3 and 23.6%

Recrystallisation of the Compounds

On recrystallisation from aqueous solutions, $\text{NH}_4\text{Hg}(\text{CN})_2\text{Cl}$ appears to undergo some decomposition and is gradually contaminated with greater quantities of mercuric cyanide. For example, recrystallisation of the compound gave a product corresponding to the empirical formula $\text{NH}_4\text{Hg}(\text{CN})_2\text{Cl} \cdot 0.75\text{Hg}(\text{CN})_2$; a second recrystallisation gave $\text{NH}_4\text{Hg}(\text{CN})_2\text{Cl} \cdot 2\text{Hg}(\text{CN})_2 \cdot \text{LiHg}(\text{CN})_2\text{Cl}$ on recrystallisation gave mercuric cyanide. The other compounds did not change in composition on recrystallisation. These results indicate that the chloride complexes are the least stable.

One of us (A. K. A.) is grateful to the C. S. I. R., New Delhi for a Junior Research Fellowship during the tenure of which the above investigations were carried out.

Gorakhpur (India), Chemical Laboratories University of Gorakhpur.

Bei der Redaktion eingegangen am 24. November 1962.